

THE HYDROGENATION OF CARBON MONOXIDE OVER RANEY IRON-MANGANESE CATALYSTS

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INTRODUCTION

The hydrogenation of carbon monoxide for the synthesis of hydrocarbons was extensively investigated in Germany beginning in the 1920s⁽¹⁾ and in the United States during the 1950s.⁽²⁾ These early studies focused on the production of liquid hydrocarbons and methane and very little attention was paid to the synthesis of low-molecular weight hydrocarbons such as ethane, ethylene, propane, butane and butylenes.

Coprecipitated iron-manganese catalysts⁽³⁾ gave favorable selectivity for low molecular weight olefins. This preliminary investigation⁽³⁾ was extended to include process variable and reactor studies using coprecipitated iron-manganese catalysts.⁽⁴⁻⁶⁾

Raney alloy catalysts, first developed by Raney⁽⁷⁾, have been used in applications where high activity and selectivity were required in hydrogenation reactions.⁽⁷⁾ Raney iron-manganese catalysts have recently been studied to determine their selectivity towards low molecular weight C_2 - C_4 olefins.⁽⁸⁾

The objective of this investigation was to determine the optimum operating conditions for the production of low-molecular weight olefins over Raney iron-manganese catalysts.

EXPERIMENTAL APPARATUS AND PROCEDURES

Raney Alloy Preparation

The individual metal components; aluminum, iron and manganese were weighed in the appropriate proportions: Al/Fe/Mn = 59/38/3 parts by weight, were thoroughly mixed and transferred to a carbon crucible, which was placed inside a ceramic crucible and heated by an electric furnace at 1523 K for 24 hours in flowing argon. The resulting melt was quenched to room temperature. Specific details regarding the preparation procedures have been reported elsewhere.^(8,9)

Raney Catalyst Activation

Fifty grams of the alloy (25-50 mesh) were added in 5 gram aliquots to a well-stirred tank reactor which contained a 25-weight percent solution of sodium hydroxide at 3-minute intervals to avoid a significant temperature rise in the solution. The reaction temperature was controlled at 363 ± 5 K. After all the alloy had been added to the reactor it was maintained at the leaching temperature for an additional 90 minutes in order to complete the leaching of the aluminum. The catalyst was washed with distilled

water until the pH of the decanted solution was 7.0 ± 0.3 . It was then washed three times with 95% alcohol, followed by three times with 100% alcohol. The catalyst was stored under 100% ethyl alcohol in a refrigerator for subsequent characterization and evaluation.

Catalyst Evaluation Apparatus

A fixed-bed flow reactor was used to evaluate the catalysts. The flow rates of H_2 and CO gases were controlled by mass flow meters (Union Carbide Model FM 4550) which were calibrated at different operating pressures for a variety of flow rates. A Grove loader was used as a back pressure control valve to maintain the reactor system pressure constant. Downstream from the Grove loader, the pressure dropped to the ambient pressure. A condenser at the ambient temperature and pressure was used to collect the liquid products. The condensable vapor-free product gas flow was measured with a wet test meter.

Catalyst Evaluation Unit and Operating Procedure

Approximately, 2 grams of dried catalyst was mixed with an appropriate amount of inert Denstone, wetted with water and loaded into the reactor. A hydrogen flow ($600 \text{ cm}^3/\text{min}$) was established through the catalyst bed at the ambient temperature and pressure and was maintained for 1 hour to evaporate any water from the catalyst surface. The temperature of the system was then raised to 648 K in flowing hydrogen and the catalyst was reduced for 6 hours. At the desired temperature, the reactant gas (a mixture of H_2/CO) was passed through the system and the pressure was slowly increased to the desired value. The stabilization period for a typical experiment with the Raney iron-manganese catalyst was 6 to 15 hours. When necessary, the system operating variables were changed and after the system stabilized at the new conditions (30 to 45 minutes) the product stream was sampled after an additional 10 minutes. The gas products were analyzed by a gas chromatograph (HP 5830A). A thermal conductivity detector (TCD) was used for carbon dioxide, carbon monoxide and water and a flame ionization detector (FID) was used for the hydrocarbon products up to heptanes. A Chromosorb 102 (80-100 mesh 6.1 meters) column which was capable of resolving methane through the heptanes (saturates and unsaturates), was used.

Catalyst Stability Test

The stability of Raney iron-manganese catalyst was determined in an experiment which lasted 36-40 hours. The global heat transfer problem associated with exothermic reactions in fixed-bed reactors was alleviated by loading inert Denstone with the catalyst. The density of Raney catalyst is approximately equal to 2 g/cm^3 , and 2 grams of it were used in each experiment. The amounts of Denstone diluent loaded with the catalyst in the three experiments were 1, 2, and 4 cm^3 , respectively. Thus, the volume ratios used in the stability tests were 1, 2 and 4.

Process Variable Investigation

A statistical design⁽⁹⁾ method was used in the process variable investigation with the Raney iron-manganese catalyst system. Four variables, namely, temperature, pressure, H_2/CO ratio and space velocity were selected for study. Each process operating variable was assigned five different levels: -2, -1, 0, 1 and 2. The selection of the range of operating variables was based on preliminary experimental data and on experimental design theory. The process operating conditions are listed in Table 1.

RESULTS AND DISCUSSION

Catalyst Loading and Stability Tests

The loading and stability tests were conducted to determine the range of operating conditions for the process variable investigation and to determine the effect of on-stream time on the activity, selectivity and stability of Raney iron-manganese catalysts. The carbon monoxide conversion as a function of run time at different inert diluent to catalyst ratios at 1470 KPa, 443 K, sv of $4.2 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and H_2/CO ratio of two is presented in Figure 1. It was determined that the induction period for the catalysts at three different diluent/catalyst ratios was about 15 hours. The two diluted bed experiments gave the same carbon monoxide conversions 2.8%, after 15 hours on stream. The effect of reaction temperature on the product selectivity for two different diluent/catalyst ratios at 1470 KPa, sv of $4.2 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and H_2/CO ratio of two are presented in Figures 2 and 3. The temperature had almost no effect on the yields of all products except carbon dioxide in both cases. The carbon dioxide selectivity increased as the temperature increased and the rate of increase was almost the same for both the dense and the diluted bed modes of operation; however, at a given temperature, the carbon dioxide yield for the diluted bed mode was lower than that for the dense bed mode. It was concluded from the higher operating temperature and lower carbon dioxide yields in the diluted bed mode that the surface temperature of the catalyst in dense bed mode was higher than the catalyst surface temperature in the diluted bed. Poor heat transfer in the dense bed caused a higher temperature gradient. The results of the loading and the stability test indicated that the preferred diluent to catalyst ratio was four to one.

Process Variable Investigation: C_2-C_4 Olefin Yield Response Equation

A statistical design model was used to optimize the C_2-C_4 olefin production. The second order response equation for a four variable system is written as follows:

$$Y_1 = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_{11}X_1^2 + B_{22}X_2^2 + B_{33}X_3^2 + B_{44}X_4^2 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{14}X_1X_4 + B_{23}X_2X_3 + B_{24}X_2X_4 + B_{34}X_3X_4$$

where Y_1 is the C_2-C_4 olefin to paraffin ratio response factor, X_1 is the pressure, X_2 is the temperature, X_3 is the reactant gas space velocity, and X_4 is the H_2/CO molar ratio.

The operating variables, carbon monoxide conversions and the product distributions for 25 design experiments are listed in Table 2. The carbon dioxide yield, the carbon monoxide conversion, the C_2 - C_4 hydrocarbon yield, the olefin to paraffin ratio in the C_2 - C_4 hydrocarbon fraction and the C_5^+ hydrocarbon yield were used as independent variables in the statistical design computations. The selectivities, as reflected by the olefin to paraffin ratios for the C_2 , C_3 , C_4 and C_2 - C_4 hydrocarbon fractions, are listed in Table 3. The computed response surface correlation coefficients are listed in Table 4. The F-test technique was used to determine the significance of each coefficient. Those coefficients which were determined not to be significant were eliminated. The reduced set of response surface correlation coefficients from the process variable study are listed in Table 5. The C_2 - C_4 olefin to paraffin ratio, Y_1 , can be expressed as a response surface equation from the data as follows:

$$Y_1 = 3.406 - 0.243 X_1 + 0.319 X_2 - 0.884 X_4 + 0.026 X_1^2 - 0.003 X_2^2 + 0.111 X_4^2 + 0.164 X_1 X_4 - 0.233 X_2 X_4$$

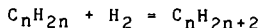
where Y_1 , X_1 , X_2 , X_3 and X_4 have been defined previously.

This equation can be used to quantitatively predict the C_2 - C_4 olefin to paraffin ratio for the range of operating variables investigated. The response surface equations for other independent variables can also be constructed using the same technique and the coefficients are presented in Table 5. In this study, the H_2/CO ratio appeared to be the most significant operating variable. The response factor for the C_2 - C_4 olefin to paraffin ratio changed by a factor of unity when the H_2/CO ratio was changed by a factor of -0.884 and thus the H_2/CO ratio was judged to be the most significant operating variable while the space velocity was the least significant operating variable influencing the olefin to paraffin ratio. Thus, the space velocity (X_3) was eliminated from the response surface equation. The first-order coefficients for the pressure and temperature terms (X_1 and X_2 , respectively) were $B_1 = -0.243$ and $B_2 = 0.319$, respectively. Since the magnitude of each is less than the magnitude of the first order coefficient for the H_2/CO ratio (X_4), $B_4 = -0.884$, the temperature and pressure are less significant with regard to the C_2 - C_4 olefin-to-paraffin ratio than the H_2/CO ratio. The first and second order coefficients for the C_2 - C_4 and C_5^+ hydrocarbon yields are considerably smaller than their respective zero order coefficients, which indicates that the yield of C_2 - C_4 and C_5^+ hydrocarbons is somewhat insensitive to the operating conditions in the range of process variables investigated.

Effect of Pressure on Product Distribution and Olefin Selectivity

The carbon monoxide conversion decreased as the pressure decreased. At a temperature of 463 K, a space velocity of $9 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and a H_2/CO ratio of one, the carbon monoxide conversion decreased from 4% at 4230 KPa to 2.8% at 1470 KPa. At a temperature of 473 K, a space velocity of $12 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and H_2/CO ratio of two, the carbon monoxide conversion decreased from 6.3% at 3540 KPa to 5.7% at 2160 KPa. This decrease may be due to a change in the carbon monoxide surface coverage brought about by the pressure

decrease. The C_2 - C_4 olefin to paraffin ratio decreased from 3.8 at 1470 KPa to 2.7 at 4230 KPa. The carbon dioxide, C_2 - C_4 hydrocarbons, and C_5^+ hydrocarbon yields remained almost constant in the pressure range from 1470 to 4230 KPa. The olefin to paraffin ratios for the C_2 , C_3 , C_4 and C_2 - C_4 hydrocarbon fractions also decreased as the pressure increased. The olefin to paraffin ratios for the C_2 and C_3 hydrocarbon fractions were consistently higher than that of the C_4 hydrocarbon fraction in the pressure range investigated: 1470 KPa to 4230 KPa. At a reaction temperature of 453 K, a space velocity of $9 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and a H_2/CO ratio of 1, the olefin to paraffin ratios for the C_2 , C_3 , C_4 fraction increased from 3.7, 2.8 and 2.1 at 4230 KPa to 4.2, 3.7 and 3.8 at 1470 KPa, respectively. It is obvious from the stoichiometric equation for the olefin hydrogenation reaction:



that the olefinic products are favored at lower pressure.

Effect of Temperature on Product Distribution and Olefin Selectivity

The carbon monoxide conversion increased as the temperature increased at a reaction pressure of 3540 KPa, a space velocity of $12 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and a H_2/CO of two; that is, the carbon monoxide conversion increased from 5.4% at 453 K to 6.3% at 473 K. The C_2 - C_4 olefin to paraffin ratio increased from 2.8 to 3.7 as the temperatures increased from 443 to 483 K. The olefin to paraffin ratios of the C_3 and C_4 fraction increased as the temperature increased, whereas the olefin to paraffin ratio of the C_2 to C_3 hydrocarbon fractions was consistently higher than that of the C_4 hydrocarbon fraction in the temperature range investigated, 443 to 483 K. At a pressure of 2850 KPa, a space velocity of $9 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ and a H_2/CO ratio of 1, the olefin to paraffin ratios of C_2 , C_3 and C_4 increased from 4.1, 2.5 and 1.9 at 443 K to 4.3, 3.8 and 3.3 at 483 K, respectively. The carbon dioxide selectivity increased as the temperature increased. This is consistent with the observations made in connection with the catalyst loading and stability tests.

Effect of Reactant Gas Space Velocity on Product Distribution and Olefin Selectivity

The carbon monoxide conversion decreased as the space velocity increased (Table 2). At higher space velocities, the contact time between reactant species and the catalyst surface was reduced. The shorter contact time resulted in lower carbon monoxide conversion. At a pressure of 3540 KPa, a temperature of 453 K and a H_2/CO ratio of two, the carbon monoxide conversion increased from 3.6% to 5.4% as the space velocity decreased from $12 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ to $6 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$. The olefin to paraffin ratios of C_2 , C_3 , C_4 , and C_2 - C_4 hydrocarbon fractions remained constant in the range of space velocities from 3 to $15 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$. The olefin to paraffin ratios of the C_2 and C_3 hydrocarbon fractions were consistently higher than that of the C_4 hydrocarbon fraction in the range of space velocities from 3 to $15 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$. At other operating conditions, the olefin to paraffin ratios were the same at space velocities of 6 and $12 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$. The yields of the C_2 - C_4 and C_5 hydrocarbon yields were independent of space velocity. The carbon dioxide yield decreased from 50% at a

space velocity of $3 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ to 27% at a space velocity of $15 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$. As mentioned in the stability test section, the high space velocity suppresses the Boudouard and water gas shift reactions, thus leading to a decrease in carbon dioxide production.

Effect of Hydrogen to Carbon Monoxide Ratio on Product Distribution and Olefin Selectivity

The carbon monoxide conversion decreased as the H_2/CO ratio decreased (Table 2). At a pressure of 2850 KPa, a temperature of 463 K and a space velocity of $9 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ the carbon monoxide conversion decreased sharply from 14.5 % at a H_2/CO ratio of 5 to 0.9 % at a H_2/CO ratio of 0.2. The olefin to paraffin ratios of the C_2 , C_3 , C_4 , and $\text{C}_2\text{-C}_4$ hydrocarbon fractions were very sensitive to the H_2/CO ratio (Table 3). At a constant total pressure a reduction in the hydrogen to carbon monoxide ratio reduces the hydrogen partial pressure in the reactor thus favoring the formation of olefins. The carbon dioxide yield also increased to some extent at the hydrogen to carbon monoxide ratio decreased indicating the rate of the Boudouard reaction increased with lower hydrogen to carbon monoxide ratio.

Interaction of Process Variable

The $\text{C}_2\text{-C}_4$ olefin to paraffin ratios were influenced by the process variables: temperature, pressure and H_2/CO ratio. The coefficient B_{14} represents the interaction between the pressure and the H_2/CO ratio and was equal to 0.164. Thus, whenever the total pressure or the H_2/CO ratio was changed by one level, the olefin to paraffin ratio in the $\text{C}_2\text{-C}_4$ hydrocarbon fraction changed by an amount corresponding to a value of 0.164. The coefficient B_{24} represents the interaction between temperature and the H_2/CO ratio and was equal to -0.223. Thus, whenever the reactor temperature or the H_2/CO ratio is changed one level, the olefin to paraffin ratio in the $\text{C}_2\text{-C}_4$ hydrocarbon fraction changes by an amount corresponding to a value of 0.223. The retention of interactive terms B_{14} and B_{24} , after the analysis of the coefficients is probably related to the influence of pressure, temperature and H_2/CO ratio on the fraction of the surface covered by the reacting species, hydrogen and carbon monoxide and on the ratio of the fraction of the surface covered by each.

Statistical Model

The $\text{C}_2\text{-C}_4$ olefin to paraffin ratio, displayed as a function of process variables, taken two at a time, predicted from the statistical design are presented in Figures 4 and 5. These figures were prepared using a commercial (Golden Graphics) software package (11) on an IBM PC AT. The inverse distance squared algorithm was selected for the grid calculation. (12) the calculation conditions: grid size 21, smooth factor 0.95, view angle 60 degrees, rotation angle 225 degrees, and height/width ratio of one were selected to better display the response surfaces. The variable dependence can be understood by comparing the slopes of the two lines AB and AC in Figure 4. The rate of change of AC as a function of the H_2/CO ratio is greater than that of AB as a function of pressure. The smooth response surface obtained from the correlation

at least indicates that the reaction conditions used in this investigation are reasonable and the predicted model can be extended to other process variables.

Optimum Process Operating Conditions

The process operating conditions required to produce the optimal C_2 - C_4 hydrocarbon fraction, olefin to paraffin ratio, were computed using the calculated coefficients for the response surface as the input data. As discussed, a lower H_2/CO ratio, a higher temperature and a lower pressure would be expected to produce a higher olefin to paraffin ratio in the C_2 - C_4 hydrocarbon fraction. The H_2/CO ratio is limited to a minimum value of 0.5 in the experiment to avoid excessive carbon deposition on the catalyst. The optimal operating conditions and the C_2 - C_4 olefin to paraffin ratios predicted from the response surface equation were: a pressure of 1470 KPa, a temperature of 473 K, a space velocity of $12 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$, a H_2/CO ratio of 0.5 and an olefin to paraffin ratio of 5.4. At the predicted optimal operating conditions, an olefin to paraffin ratio of 6.4 was obtained, which was higher than expected. At the optimal operating conditions, the olefin to paraffin ratios for the C_2 , C_3 and C_4 hydrocarbon fractions were as follows: the ethylene to ethane ratio was 5, the propylene to propane ratio of 9.3 and the butylenes to butanes was 5.2.

CONCLUSIONS

1. The activity as reflected by carbon monoxide conversion and the selectivity as reflected by the C_2 - C_4 olefin to paraffin ratio of the Raney iron-manganese catalyst were constant up to 40 hours on stream.
2. The most influential operating variable in determining the olefin selectivity is the H_2/CO ratio.
3. The optimal operating conditions for the maximization of low molecular weight olefins were: a temperature of 473 K, a sv of $12 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$, a H_2/CO ratio of 0.5 and a pressure of 1470 KPa. The olefin to paraffin ratio at these conditions is 6.4.

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REFERENCES

1. Storch, H. H., Couloumbic, N. and Anderson, R. B., The Fischer-Tropsch and Related Synthesis, Wiley, New York, 1951.
2. Gryson, M., Demeter, J. J., Schkesinger, M. D., Johnson, G. E., and Myers, J. W., Synthesis of Methane," Report of Investigations 5137, Bureau of Mines, 1955.

3. Yang, C. H., "Catalytic Synthesis of Light Hydrocarbons from Carbon Monoxide and Hydrogen over Metal Catalysts," Ph.D. Dissertation, University of Utah, Department of Mining and Fuels Engineering, 1979.
4. Tsai, Y. S., "The Hydrogenation of Carbon Monoxide over Unsupported Iron/Manganese Catalysts to Produce Low Molecular Weight Olefins," Master Thesis, University of Utah, Department of Mining and Fuels Engineering, 1980.
5. Tai, W. P., "The Hydrogenation of Carbon Monoxide over Coprecipitated Iron/Manganese Catalyst in a Pseudo Slurry Reactor," Ph.D. Dissertation, University of Utah, Department of Mining and Fuels Engineering, 1983.
6. Tsai, Y.S., "The Synthesis of Low Molecular Weight Olefins over Co-Precipitated Iron/Manganese Catalysts", Ph.D. Dissertation, Univ. of Utah, Dept. of Fuels Engineering (1985).
7. Raney, M., "Catalysts from Alloys," Ind. Eng. Chem., 1940, 32, 1199.
8. Kim, C. S., "The Hydrogenation of Carbon Monoxide over Raney Iron-Manganese Catalysts," Ph.D. Dissertation, University of Utah, Department of Fuels Engineering, 1983.
9. Chen, K. R., "The Hydrogenation of Carbon Monoxide over Raney Iron/Manganese Catalysts: Process Variable Investigation", M.S. Thesis, University of Utah, Department of Fuels Engineering (1985).
10. Box, G. E. P. and Wilson, K. B., "On the Experimental Attainment of Optimum Conditions," J. of the Royal Stat. Soc. (series B), 1951, 13, 1.
11. Golden Graphics System Version 2. Golden Software, Inc., Colorado, 1985.
12. Ripley, B. D., Spatial Statistics, Wiley, New York, 1981.

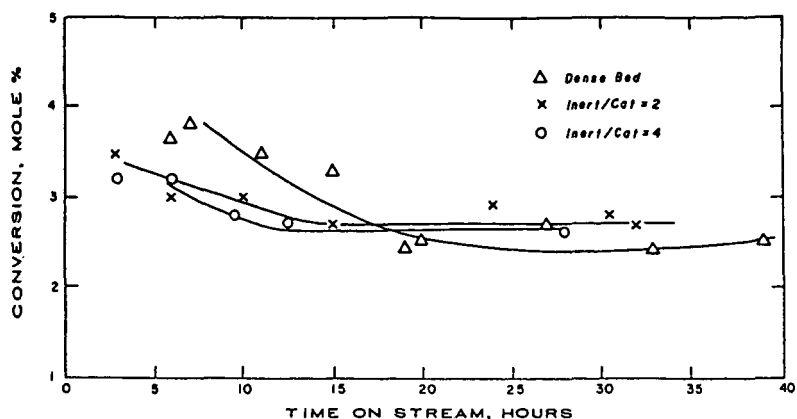


Figure 1 Catalyst Stability Test: Carbon Monoxide Conversion
 Raney Fe/Mn Catalyst; $T = 443 \text{ K}$; $P = 1470 \text{ KPa}$;
 $\text{H}_2/\text{CO} = 2/1$; Space Velocity = $4.2 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$

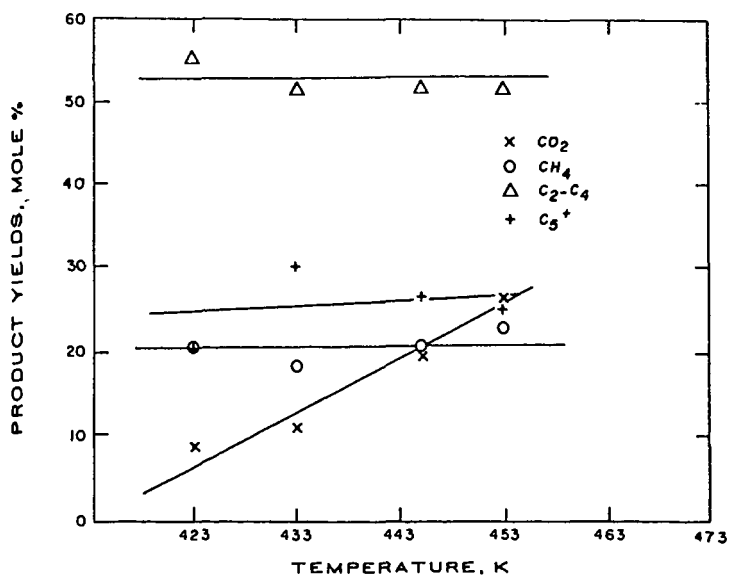


Figure 2 Effect of Temperature on Product Distribution
 Raney Fe/Mn Catalyst; $P = 1470 \text{ KPa}$, $\text{H}_2/\text{CO} = 2/1$
 Space Velocity = $4.2 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$; Diluent/Catalyst
 Ratio = 0/1

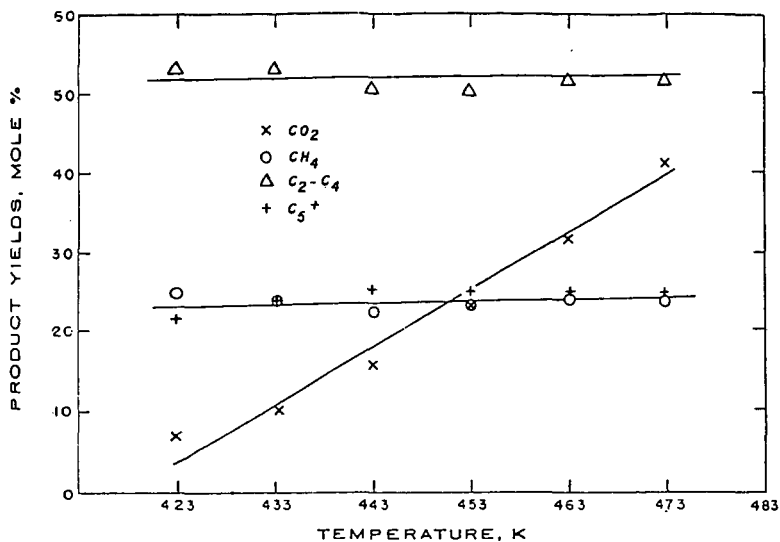


Figure 3 Effect of Temperature on Product Distribution
 Raney Fe/Mn Catalyst, $P = 1470$ KPa, $\text{H}_2/\text{CO} = 2/1$
 Space Velocity = $4.2 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$; Diluent/Catalyst
 Ratio = 4/1

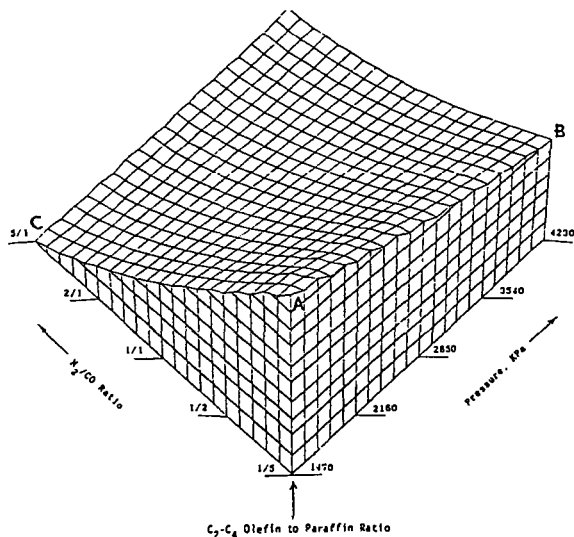


Figure 4 $\text{C}_2\text{-C}_4$ Olefin to Paraffin Ratio as a Function of
 H_2/CO Ratio and Pressure at 463 K

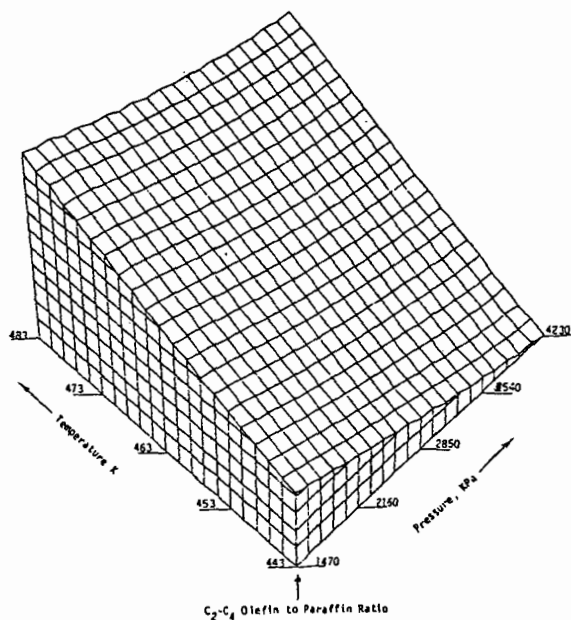


Figure 5 C₂-C₄ Olefin to Paraffin Ratio as a Function of Temperature and Pressure at a H₂/CO Ratio of Unity

Table 1

Range of Process Operating Conditions for
Process Variable Study

Variable Level	-2	-1	0	1	2	Range ⁽¹⁾
Temperature, K	443	453	463	473	483	10
Pressure, KPa	1470	2160	2850	3540	4230	690
Hydrogen to Carbon Monoxide Ratio	5/1	2/1	1/1	1/2	1/5	1/2
Space Velocity, cm ³ g ⁻¹ s ⁻¹	3	6	9	12	15	3

(1) Range = $\frac{\text{Condition}(2) - \text{Condition}(1)}{4}$

Table 2

Carbon Monoxide Conversion and Product Distribution
Process Variable Investigation

Raney Iron/Manganese (16/1) Catalyst

Run No.	Pressure (KPa)	Temperature (K)	Space Velocity ($\text{cm}^3\text{g}^{-1}\text{s}^{-1}$)	Hydrogen/Carbon Monoxide Ratio	Carbon Monoxide Conversion (mol %)	Product Distribution (mol %)			
						C ₁	C ₂ -C ₄	C ₅ ⁺	CO ₂
1	3540	473	12	2/1	6.3	0.19	0.53	0.27	0.18
2	3540	473	12	1/2	2.2	0.15	0.54	0.31	0.27
3	3540	473	6	2/1	13.3	0.18	0.53	0.28	0.22
4	3540	473	6	1/2	5.7	0.14	0.55	0.30	0.51
5	3540	453	12	2/1	3.6	0.19	0.55	0.26	0.15
6	3540	453	12	1/2	1.2	0.17	0.49	0.29	0.38
7	3540	453	6	2/1	5.4	0.20	0.53	0.26	0.11
8	3540	453	6	1/2	1.8	0.15	0.50	0.31	0.30
9	2160	473	12	2/1	5.8	0.22	0.52	0.26	0.24
10	2160	473	12	1/2	1.8	0.17	0.51	0.32	0.32
11	2160	473	6	2/1	11.2	0.21	0.52	0.26	0.29
12	2160	473	6	1/2	2.5	0.16	0.53	0.31	0.23
13	2160	453	12	2/1	2.7	0.23	0.53	0.24	0.12
14	2160	453	12	1/2	1.1	0.19	0.45	0.31	0.44
15	2160	453	6	2/1	4.6	0.22	0.52	0.26	0.15
16	2160	453	6	1/2	1.5	0.17	0.49	0.29	0.29
17	4230	463	9	1/1	4.0	0.16	0.56	0.27	0.32
18	1470	463	9	1/1	2.8	0.20	0.50	0.29	0.31
19	2850	483	9	1/1	11.9	0.17	0.55	0.28	0.52
20	2840	443	9	1/1	0.9	0.20	0.49	0.25	0.09
21	2850	463	15	1/1	2.5	0.18	0.49	0.29	0.27
22	2850	453	3	1/1	13.6	0.16	0.56	0.27	0.51
23	2850	463	9	5/1	14.5	0.27	0.50	0.22	0.15
24	2850	463	9	1/5	0.9	0.19	0.53	0.28	0.61
25	2850	463	9	1/1	3.0	0.18	0.53	0.30	0.33

Table 3

C₂, C₃, C₄ and C₂-C₄ Olefin Selectivity
Process Variable Investigation

Raney Iron/Manganese (16/1) Catalyst

Run No.	Pressure (KPa)	Temperature (K)	Space Velocity (cm ³ g ⁻¹ s ⁻¹)	Hydrogen/Carbon Monoxide Ratio	Carbon Monoxide Conversion (mol %)	Olefin to Paraffin Ratio			
						C ₂	C ₃	C ₄	C ₂ -C ₄
1	3540	473	12	2/1	6.3	1.9	2.8	2.1	2.3
2	3540	473	12	1/2	2.2	5.0	4.3	3.5	4.0
3	3540	473	6	2/1	13.3	1.9	2.9	2.7	2.5
4	3540	473	6	1/2	5.7	5.0	4.3	3.2	4.0
5	3540	453	12	2/1	3.6	2.4	2.3	1.8	2.1
6	3540	453	12	1/2	1.2	4.8	3.2	2.3	3.1
7	3540	453	6	2/1	5.4	2.1	2.3	1.7	2.0
8	3540	453	6	1/2	1.8	4.6	3.1	2.3	3.1
9	2160	473	12	2/1	5.8	1.5	3.4	2.5	2.4
10	2160	473	12	1/2	1.8	5.4	5.6	4.3	5.1
11	2160	473	6	2/1	11.2	1.5	3.5	2.6	2.5
12	2160	473	6	1/2	2.5	5.2	5.6	4.1	4.9
13	2160	453	12	2/1	2.7	2.2	2.8	2.1	2.4
14	2160	453	12	1/2	1.1	5.6	3.8	2.8	3.7
15	2160	453	6	2/1	4.7	2.0	2.7	2.0	2.4
16	2160	453	6	1/2	1.5	5.4	3.8	2.8	3.7
17	4230	463	9	1/1	4.0	3.7	2.8	2.1	2.7
18	1470	463	9	1/1	2.8	4.1	4.2	3.7	3.8
19	2850	443	9	1/1	11.9	4.3	3.8	3.3	3.8
20	2840	443	9	1/1	0.9	4.1	2.5	1.9	2.6
21	2850	463	15	1/1	2.5	3.9	3.1	2.4	3.0
22	2850	451	3	1/1	13.6	3.3	3.4	2.3	3.0
23	2850	463	9	5/1	14.5	0.9	2.3	1.7	1.6
24	2850	463	9	1/5	0.9	7.1	5.9	4.4	5.6
25	2850	463	9	1/1	3.3	3.5	3.6	2.8	3.3

Table 4
Correlation Coefficients from the Process Variable Investigation

$\beta_i^{(1)}$	C_2-C_4 Olefin/Paraffin Ratio	Product Yields			
		C_1	C_2-C_4	C_5^+ Hydrocarbons	Carbon Dioxide
β_0	3.310	0.180	0.530	0.300	0.380
β_1	-2.43	-0.012	0.011	-0.001	0.003
β_2	0.319	-0.007	0.012	0.006	0.049
β_3	-0.007	0.006	-0.010	0.001	-0.023
β_4	-0.884	0.021	0.004	-0.019	-0.092
β_{11}	-0.034	-0.001	-0.001	-0.002	-0.030
β_{22}	-0.057	0.000	-0.003	-0.006	-0.033
β_{33}	-0.093	-0.004	-0.002	-0.002	-0.002
β_{44}	0.051	0.011	-0.004	-0.010	-0.014
β_{12}	-0.019	0.000	0.001	0.000	0.010
β_{13}	-0.033	0.000	0.001	-0.001	-0.025
β_{14}	0.164	-0.003	-0.002	0.004	-0.020
β_{23}	-0.223	0.001	-0.014	0.000	0.030
β_{34}	-0.031	-0.001	0.005	0.004	-0.015

(1) β_1 : pressure, β_2 : temperature, β_3 : space velocity
 β_4 : hydrogen to carbon monoxide ratio

Table 5
Reduced Correlation Coefficients from the
Process Variable Investigation

$\beta_i^{(1)}$	C_2-C_4 Olefin/Paraffin Ratio	Product Yields			
		C_1	C_2-C_4	C_5^+ Hydrocarbons	Carbon Dioxide
β_0	3.047	0.180	0.520	2.910	0.308
β_1	-0.243	-0.012	0.011
β_2	0.319	0.07	0.012	0.006	0.048
β_3	0.006	-0.010	-0.023
β_4	-0.884	0.021	-0.019	-0.092
β_{11}	0.026
β_{22}	0.003	-0.004	-0.016
β_{33}
β_{44}	0.111	0.011	-0.008	0.002
β_{12}
β_{13}
β_{14}	0.164
β_{23}
β_{24}	-0.223	-0.014
β_{34}

(1) β_1 : pressure, β_2 : temperature, β_3 : space velocity
 β_4 : hydrogen to carbon monoxide ratio